

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 December 2001 (27.12.2001)

PCT

(10) International Publication Number
WO 01/98240 A2

(51) International Patent Classification⁷: C07C 19/08,
17/20, 17/10

(21) International Application Number: PCT/JP01/05256

(22) International Filing Date: 20 June 2001 (20.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2000-185654 21 June 2000 (21.06.2000) JP
60/230,806 7 September 2000 (07.09.2000) US

(71) Applicant (*for all designated States except US*): SHOWA
DENKO K.K. [JP/JP]; 13-9, Shibadaimon 1-chome, Mi-
nato-ku, Tokyo 105-8518 (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): OHNO, Hiromoto
[JP/JP]; c/o KAWASAKI PLANT, SHOWA DENKO
K.K., 5-1, Ogimachi, Kawasaki-ku, Kawasaki-shi, Kana-
gawa 210-0867 (JP). KAGA, Kazunari [JP/JP]; c/o
KAWASAKI PLANT, SHOWA DENKO K.K., 5-1, Ogi-
machi, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0867
(JP). OHI, Toshio [JP/JP]; c/o KAWASAKI PLANT,
SHOWA DENKO K.K., 5-1, Ogimachi, Kawasaki-ku,
Kawasaki-shi, Kanagawa 210-0867 (JP).

(74) Agent: SUZUKI, Shunichiro; SUZUKI & ASSO-
CIATES, Gotanda Yamazaki Bldg. 6F, 13-6, Nishigotanda
7-chome, Shinagawa-ku, Tokyo 141-0031 (JP).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA,
ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: PROCESS FOR PRODUCING HEXAFLUOROETHANE AND USE THEREOF

(57) Abstract: The present invention intends to provide a process for producing CF_3CF_3 with good profitability using CF_3HF_2 con-
taining a compound having chlorine atom within the molecule, and use thereof. In the process of the present invention, a gas mixture
containing CF_3CHF_2 and a compound having chlorine atom within the molecule is reacted with hydrogen fluoride in the presence of
a fluorination catalyst, thereby converting CClF_2CF_3 as a main impurity into CF_3CF_3 , and CF_3CHF_2 containing CF_3CF_3 is reacted
with fluorine gas in the gaseous phase in the presence of a diluting gas.

WO 01/98240 A2

DESCRIPTION

Process for Producing Hexafluoroethane and Use Thereof

5

CROSS REFERENCE TO RELATED APPLICATION

This application is an application filed under 35 U.S.C. § 111(a) claiming benefit pursuant to 35 U.S.C. § 119(e)(1) of the filing date of Provisional Application 60/230,806 filed on September 7, 2000, pursuant to 35 U.S.C. § 111(b).

10

DETAILED DESCRIPTION OF THE INVENTION

Technical Field of the Invention

15

The present invention relates to a process for producing hexafluoroethane, comprising a step of reacting a gas mixture containing pentafluoroethane and a compound having chlorine atom with hydrogen fluoride in the gaseous phase in the presence of a fluorination catalyst to fluorinate the compound having chlorine atom and a step of reacting the gas mixture containing pentafluoroethane and the fluorinated compound with fluorine gas in the gaseous phase in the presence of a diluting gas, and also relates to the use thereof.

20

25

Background Art

Pentafluoroethane (hereinafter referred to as "CF₃CHF₂") is used, for example, as a refrigerant for low-temperature use or a starting material for the production of hexafluoroethane (hereinafter referred to as "CF₃CF₃").

For the production of CF₃CHF₂, for example, the following methods have been heretofore known:

- (1) a method of fluorinating perchloroethylene (CCl₂=CCl₂) or a fluoride thereof with hydrogen fluoride (see, JP-A-5-97724 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-6-506221, JP-A-7-76534, JP-A-7-118182, JP-A-8-268932 and JP-A-9-511515),
- (2) a method of performing hydrogenolysis of chloropentafluoroethane (CClF₂CF₃), and
- (3) a method of reacting a fluorine gas with a halogen-containing ethylene (see, JP-A-1-38034).

When these methods for producing CF₃CHF₂ are used, the objective CF₃CHF₂ contains a compound having chlorine atom within the molecule as main impurities. The compound having chlorine atom within the molecule includes a compound having one carbon atom within the molecule, such as chloromethane, chlorodifluoromethane and chlorotrifluoromethane, a compound having two carbon atoms within the molecule, such as chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane and

chlorotrifluoroethane, and an unsaturated compound such as chlorotrifluoroethylene.

In the case of producing CF_3CF_3 by a direct fluorination reaction of reacting CF_3CHF_2 with a fluorine gas (F_2), if CF_3CHF_2 contains the compound having chlorine atom within the molecule, chlorine, hydrogen chloride, chlorine fluoride or different kinds of chlorofluorocarbons are generated in the reaction with fluorine gas. Even when hydrofluorocarbons (HFC) or perfluorocarbons (PFC) are contained in CF_3CHF_2 , there arises no particular problem, however, for example, chloromethane (CH_3Cl) or chlorodifluoromethane (CHClF_2) reacts with fluorine gas to produce chlorotrifluoromethane (CClF_3). The objective CF_3CF_3 and chlorotrifluoromethane form an azeotropic composition, therefore, CClF_3 is difficult to remove even by performing distillation, adsorption for purification, or the like. Accordingly, in the case of reacting CF_3CHF_2 with a fluorine gas to produce CF_3CF_3 , the amount of the compound having chlorine atom within the molecule contained in CF_3CHF_2 should be reduced as much as possible.

According to conventional production methods for CF_3CHF_2 , the total amount of the compound having chlorine atom within the molecule is sometimes as high as about 1 vol%. Therefore, a distillation operation is repeated for removing these compounds contained in CF_3CHF_2 and elevating the purity of CF_3CHF_2 , however,

this has such a problem that the distillation cost increases, the distillation loss is caused, the profitability is bad and some compounds having chlorine atom within the molecule form an azeotropic mixture or an azeotrope-like mixture with CF_3CHF_2 and are very difficult to remove only by the distillation operation. In particular, chloropentafluoroethane (hereinafter referred to as " CClF_2CF_3 ") is usually contained in CF_3CHF_2 in a concentration of thousands of ppm or more but since an azeotropic mixture is formed by CF_3CHF_2 and CClF_2CF_3 , the separation is hardly attained by distillation which is a commonly used separation and purification method.

For separating CClF_2CF_3 contained in CF_3CHF_2 , various methods have been proposed, for example,

(1) a method of adding a third component to a mixture of CF_3CHF_2 and CClF_2CF_3 and performing the extractive distillation (see, JP-A-6-510980, JP-A-7-133240, JP-A-7-258123, JP-A-8-3082, JP-A-8-143486 and JP-A-10-513190),

(2) a method of removing CClF_2CF_3 contained in CF_3CHF_2 using an adsorbent (see, JP-A-6-92879 and JP-W-8-508479 (the term "JP-W" as used herein means an "unexamined published international patent application")), and

(3) a method of converting CClF_2CF_3 contained in CF_3CHF_2 into CF_3CHF_2 in the presence of a hydrogenation catalyst (see, JP-A-7-509238, JP-A-8-40949, JP-A-8-

301801 and JP-A-10-87525).

However, these methods have a problem, that is, the method of (1) requires a step of recovering the third component from the mixture of CClF_2CF_3 and the
5 third component, the method of (2) requires a step of regenerating the adsorbent, and the method of (3) suffers from reduction in the catalytic life due to hydrogen chloride produced.

10 Problems to be Solved by the Invention

The present invention has been made under these circumstances and the object of the present invention is to provide a method for producing CF_3CF_3 with good profitability using a gas mixture containing CF_3CHF_2
15 and a compound having chlorine atom within the molecule in the method for producing CF_3CF_3 which is used as an etching or cleaning gas in the process of producing a semiconductor device, and also provide a use thereof.

20

Means to Solve the Problems

As a result of extensive investigations to solve the above-described problems, the present inventors have found that in the method for producing CF_3CF_3 ,
25 when a gas mixture containing CF_3CHF_2 and a compound having chlorine atom within the molecule as impurities is reacted with hydrogen fluoride in the presence of a fluorination catalyst to convert CClF_2CF_3 which is

contained in the gas mixture, into CF_3CF_3 and then performing a direct fluorination reaction of reacting the resulting gas mixture containing CF_3CHF_2 and CF_3CF_3 with a fluorine gas in the gaseous phase in the presence of a diluting gas, the above-described problems can be solved. The present invention has been accomplished based on this finding. The present invention provides a process for producing CF_3CF_3 and use thereof, described in [1] to [19] below.

[1] A process for producing hexafluoroethane, comprising the following two steps:

(1) a step of reacting a gas mixture containing pentafluoroethane and a compound having chlorine atom with hydrogen fluoride in the gaseous phase in the presence of a fluorination catalyst to fluorinate the compound having chlorine atom; and

(2) a step of reacting the gas mixture containing pentafluoroethane and the fluorinated compound obtained in the step (1) with a fluorine gas in the gaseous phase in the presence of a diluting gas.

[2] The process for producing hexafluoroethane as described in [1], wherein the compound having chlorine atom is at least one compound selected from the group consisting of chloromethane, chlorotrifluoromethane, chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane, chlorotrifluoroethane and chlorotrifluoroethylene.

[3] The process for producing hexafluoroethane as

described in [1] or [2], wherein the total amount of the compound having chlorine atom contained in the gas mixture of the step (1) is 1 vol% or less.

5 [4] The process for producing hexafluoroethane as described in [1] or [2], wherein the total amount of the compound having chlorine atom contained in the gas mixture of the step (1) is 0.5 vol% or less.

10 [5] The process for producing hexafluoroethane as described in any one of [1] to [4], wherein in the step (1), the fluorination catalyst is a bulk catalyst obtained by adding indium to an oxide of chromium.

15 [6] The process for producing hexafluoroethane as described in any one of [1] to [5], wherein in the step (1), the temperature at the reaction with hydrogen fluoride in the presence of a fluorination catalyst is in the range of 150 to 480°C.

20 [7] The process for producing hexafluoroethane as described in any one of [1] to [6], wherein in the step (1), the molar ratio of hydrogen fluoride/organic substance contained in the gas mixture is in the range of 0.5 to 5.

25 [8] The process for producing hexafluoroethane as described in any one of [1] to [7], wherein a step of removing an acid content containing hydrogen chloride produced is conducted before the step (2).

[9] The process for producing hexafluoroethane as described in any one of [1] to [8], wherein a step of separating chlorotetrafluoroethane and/or chlorotri-

fluoroethane, and returning the chlorotetrafluoroethane and/or chlorotrifluoroethane separated to the step (1) is conducted before the step (2).

5 [10] The process for producing hexafluoroethane as described in any one of [1] to [9], wherein in the step (2), the total amount of the compound having chlorine atom contained in the gas mixture is 0.02 vol% or less.

10 [11] The process for producing hexafluoroethane as described in any one of [1] to [10], wherein in the step (2), the fluorinated compound contained in the gas mixture is mainly composed of hexafluoroethane.

15 [12] The process for producing hexafluoroethane as described in any one of [1] to [11], wherein in the step (2), the diluting gas is a gas containing at least one selected from the group consisting of tetrafluoromethane, hexafluoroethane, octafluoropropane and hydrogen fluoride.

20 [13] The process for producing hexafluoroethane as described in any one of [1] to [12], wherein in the step (2), the diluting gas is a gas rich in hydrogen fluoride.

25 [14] The process for producing hexafluoroethane as described in any one of [1] to [13], wherein in the step (2), the temperature at the reaction of gas mixture containing the fluorinated compound with fluorine gas is in the range of 250 to 500°C.

[15] The process for producing hexafluoroethane as described in any one of [1] to [14], wherein in the

step (2), the temperature at the reaction of gas mixture containing the fluorinated compound with fluorine gas is in the range of 350 to 450°C.

5 [16] A hexafluoroethane product comprising hexafluoroethane having a purity of 99.9997 vol% or more.

[17] The hexafluoroethane product as described in [16], wherein the content of the compound having chlorine atom is 1 volppm or less and the content of the pentafluoroethane is 1 volppm or less.

[18] An etching gas comprising the hexafluoroethane product described in [16] or [17].

[19] A cleaning gas comprising the hexafluoroethane product described in [16] or [17].

15 In summary, the present invention provides "a process for producing CF_3CF_3 , comprising a step of reacting a gas mixture containing CF_3CHF_2 and a compound having chlorine atom with hydrogen fluoride in the gaseous phase in the presence of a fluorination catalyst to fluorinate the compound having chlorine atom and a step of reacting a gas mixture containing CF_3CHF_2 and the fluorinated compound obtained by the above-described step with a fluorine gas in the gaseous phase in the presence of a diluting gas", "an CF_3CF_3 product comprising CF_3CF_3 having a purity of 99.9997 vol% or more", "an etching gas comprising the above-described CF_3CF_3 product" and "a cleaning gas comprising the above-described CF_3CF_3 product".

Mode for Carry Out the Invention

The production process for CF_3CF_3 and use thereof according to the present invention are described in detail below.

As described above, CF_3CHF_2 for use in the present invention is generally produced by fluorinating perchloroethylene ($\text{CCl}_2=\text{CCl}_2$) or a fluoride thereof with hydrogen fluoride (HF), and CF_3CHF_2 contains a compound having chlorine atom derived from the starting material, such as chloromethane, chlorodifluoromethane, chlorotrifluoromethane, chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane and chlorotrifluoroethane. In order to purify CF_3CHF_2 containing these compounds to a high purity, known methods by a distillation operation are employed, however, these methods have such a problem that these are not economical since the compound and CF_3CHF_2 form an azeotropic mixture or an azeotrope-like mixture, the purification by separation is very difficult, the number of stages of the distillation tower or the number of the distillation towers must be increased, and the cost for equipment or energy increases.

In the present invention, the compound having chlorine atom contained in CF_3CHF_2 as impurities is fluorinated with hydrogen fluoride at an elevated temperature in the presence of a fluorination catalyst and thereby converted into hydrofluorocarbon (HFC) or

perfluorocarbon (PFC). For example, in fluorinating CClF_2CF_3 or chlorotetrafluoroethane contained as impurities in CF_3CHF_2 using hydrogen fluoride, a reaction shown by the following formula (1) or (2) takes place:



The product is HFC or PFC free of chlorine atom, and hydrogen chloride is produced as a by-product.

In the present specification, the gas mixture containing CF_3CHF_2 and the compound having chlorine atom is sometimes referred to as "starting gas mixture".

In this fluorination reaction, the compound which is converted into HFC or PFC is chloromethane, chlorodifluoromethane, chlorotrifluoromethane, chloropentafluoroethane, dichlorotetrafluoroethane, chlorotetrafluoroethane and chlorotrifluoroethane.

These compounds are usually contained in CF_3CHF_2 in a total amount of thousands of ppm or more. When the starting gas mixture containing these compounds is reacted with a fluorine gas, the methane-type compounds are converted into CClF_3 and the ethane-type compounds are converted into CClF_2CF_3 , therefore, CF_3CF_3 obtained after the reaction contains CClF_3 and CClF_2CF_3 as main impurities.

CClF_2CF_3 scarcely reacts with a fluorine gas at

low temperatures. However, according to the investigations by the present inventors, for example, at a reaction temperature of 400°C, the amount of CClF_3 produced by the decomposition of CClF_2CF_3 is 1 ppm or less when the concentration of CClF_2CF_3 contained in the starting gas mixture is about 800 ppm or less, and about 2 ppm of CClF_3 is produced when the concentration of CClF_2CF_3 exceeds about 2,000 ppm. CClF_3 forms an azeotropic mixture with CF_3CF_3 , therefore, even if the concentration is low, this compound is difficult to remove by an operation of distillation, adsorption for purification or the like. Accordingly, it is preferred that not only a compound which produces CClF_3 upon reaction with a fluorine gas is removed from CF_3CHF_2 as a starting material but also the CClF_2CF_3 content is reduced to a low concentration as much as possible.

The total amount of the compound having chlorine atom contained in the starting gas mixture for use in the present invention is preferably 1 vol% or less, more preferably 0.5 vol% or less, still more preferably 0.3 vol% or less. If the concentration of the compound having chlorine atom exceeds 1 vol%, the reaction must be performed at a high temperature and the life of the fluorination catalyst is disadvantageously shortened, moreover, a side reaction proceeds at the same time and the productivity decreases.

The fluorination catalyst comprises at least one element selected from the group consisting of chromium,

nickel, zinc, indium and gadolinium, and may be a known catalyst such as supported catalyst or bulk catalyst.

In the case of the supported catalyst, carrier is preferably an alumina and/or partially fluorinated alumina, and supporting ratio is preferably 30 wt% or less. In the case of the bulk catalyst, particularly preferred is those containing chromium as main component, and having atomic ratio of nickel, zinc, indium and/or gadolinium to chromium of 0.01 to 0.6. In the present invention, most preferred is a bulk catalyst obtained by adding indium to an oxide of chromium.

In the step of fluorinating the compound having chlorine atom, the reaction temperature is preferably from 150 to 480°C. If the reaction temperature exceeds 480°C, the reaction is adversely affected, for example, the catalyst deteriorates or a side reaction proceeds, and this is not preferred. Although it may vary depending on the concentration of the compound contained in the starting gas mixture, a preferred reaction temperature can be selected according to the kind of the compound. For example, in the reaction of CClF_2CF_3 shown in formula (1), the reaction temperature is preferably 400°C or more, and in the reaction of CF_3CHClF shown by formula (2), the reaction temperature is preferably 300°C or more.

In the case of a reaction of chlorodifluoromethane (CHClF_2) with hydrogen fluoride, a reaction shown by

the following formula (3) takes place:



5 In this reaction, the reaction temperature is preferably 150°C or more and if the reaction temperature exceeds 400°C or more, a reverse reaction disadvantageously proceeds.

10 In the step of fluorinating a compound having chlorine atom, the reaction temperature sometimes varies depending on the kind of the compound as described above. Accordingly, in the case where a plurality of compounds are contained and these are different from each other in the optimal reaction temperature region or the concentration of each compound is high, two or more units of reactors are preferably used, though one unit of a reactor is usually sufficient.

15 The amount of HF used is, in terms of the molar ratio to the organic substance of the starting gas mixture containing CF_3CHF_2 (HF/organic substance), suitably from 0.5 to 5, preferably from 0.5 to 2. If the molar ratio is less than 0.5, the reaction is hard to proceed, whereas if it exceeds 5, a large reactor is necessary and this is not profitable.

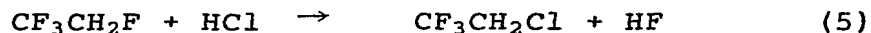
25 Furthermore, in the step of fluorinating a compound having chlorine atom, the reaction pressure is preferably from atmospheric pressure to 1.5 MPa. If it

exceeds 1.5 MPa, the apparatus is disadvantageously required to have pressure resistance or the like.

In the present invention, the reaction with hydrogen fluoride is performed in the presence of a fluorination catalyst using the above-described reaction conditions, and then CF_3CHF_2 , chlorine atom-free impurities mainly comprising HFC or PFC, and hydrogen chloride as a by-product are contained in the reaction product. In the case of CF_3CHF_2 , as the reaction temperature becomes higher, a side reaction with hydrogen chloride more proceeds as shown in the following formula (4):



In the case of containing 1,1,1,2-tetrafluoroethane, a side reaction with hydrogen chloride more proceeds as shown in the following formula (5):



Therefore, after the fluorination step of (1), the acid content containing hydrogen chloride produced is preferably removed.

The acid content is removed so as to remove unreacted hydrogen fluoride (excess hydrogen fluoride) and hydrogen chloride as a by-product. Hydrogen

fluoride brings about no adverse effect in the direct fluorination reaction step but hydrogen chloride is preferably removed because this product sometimes causes an adverse effect such as production of a chlorine-containing compound or chlorine fluoride as shown in the formula (4) or (5). The step of removing the acid content is performed before the direct fluorination reaction step. Examples of the method for removing the acid content includes:

(1) in the case of containing a large amount of unreacted hydrogen fluoride, a method of introducing an effluent containing the acid content into a distillation tower, extracting hydrogen chloride from the top and extracting organic substance and hydrogen fluoride from the bottom,

(2) a method of contacting the hydrogen chloride produced and unreacted hydrogen fluoride with a purifying agent, and

(3) a method of washing the acid content with water or alkali water.

In the present invention, the method for removing the acid content is not particularly limited and, for example, the method of (3) may be used. The alkali used therein may be an aqueous sodium hydroxide solution, an aqueous potassium hydroxide solution or the like. The absorbed hydrogen fluoride may be recovered and reused, and the gas passed through the washing solution is dehydrated using a dehydrating

agent such as zeolite.

The gas mainly comprising CF_3CHF_2 passed through the acid content-removing step sometimes contains as impurities HCFC or CFC which is not completely fluorinated by the reaction with hydrogen fluoride, and in such a case, HCFC or CFC is preferably removed by distilling before the direct fluorination reaction step.

CF_3CHF_2 and main compounds which may be contained in CF_3CHF_2 are shown, together with respective boiling points in Table 1.

Table 1

Compound Name	Structural Formula	Boiling Point ($^{\circ}\text{C}$)
Tetrafluoromethane	CF_4	-128
Trifluoromethane	CHF_3	-84
Hexafluoroethane	CF_3CF_3	-78.1
Pentafluoroethane	CF_3CHF_2	-48.5
Chloropentafluoroethane	CF_3CClF_2	-38.7
2-Chloro-1,1,1,2-tetrafluoroethane	CF_3CHClF	-12
2-Chloro-1,1,1-trifluoroethane	$\text{CF}_3\text{CH}_2\text{Cl}$	6.1

The gas mainly comprising CF_3CHF_2 is introduced into a distillation tower, then CF_4 , CHF_3 , CF_3CF_3 , CF_3CHF_2 and CClF_2CF_3 as the low boiling fraction are extracted from the top of the distillation tower, and CF_3CHClF and $\text{CF}_3\text{CH}_2\text{Cl}$ as the high boiling fraction are

extracted from the bottom. The high boiling fraction extracted from the bottom is circulated into the reaction with hydrogen fluoride of the step (1). Here, the total amount of the compound having chlorine atom, which is contained in the distillate mainly comprising CF_3CHF_2 extracted from the top, is preferably 0.02 vol% or less. The distillate mainly comprising CF_3CHF_2 is used as a starting material in the direct fluorination reaction with fluorine gas.

The step (2) of reacting the gas mainly comprising CF_3CHF_2 with fluorine gas is described below.

The step (2) is performed in the presence of a diluting gas and the gas mainly comprising CF_3CHF_2 is set to a concentration lower than the explosion range. Specifically, the CF_3CHF_2 concentration at the reactor inlet is preferably set to about 6 mol% or less. The diluting gas is a gas containing at least one selected from the group consisting of tetrafluoromethane, hexafluoroethane, octafluoropropane and hydrogen fluoride, preferably a diluting gas rich in hydrogen fluoride.

The amount of fluorine gas used is, in terms of the molar ratio to CF_3CHF_2 ($\text{F}_2/\text{CF}_3\text{CHF}_2$), suitably in the range of 0.5 to 2, preferably in the range of 0.9 to 1.3. The reaction temperature is in the range of 250 to 500°C, preferably in the range of 350 to 450°C. If the reaction temperature exceeds 500°C, the objective CF_3CF_3 is disadvantageously cleaved to produce CF_4 and

in the case of containing CClF_2CF_3 as an impurity, CClF_3 is disadvantageously produced due to cleavage of CClF_2CF_3 , whereas if it is less than 250°C , the reaction slowly proceeds and this is not preferred.

5 The method for purifying the gas distilled out from the reaction step of (2) is not particularly limited. The remaining unreacted fluorine gas may be removed by adding, for example, trifluoromethane as HFC and then the residue is distilled to separate, for
10 example, hydrogen fluoride and organic substance. The separated hydrogen fluoride is reused as the diluting gas in the direct fluorination reaction of the step (2) but may also be used as a starting material in the fluorination reaction of (1). The composition of the
15 organic substance separated greatly differs depending on the diluting gas used for the reaction and in the case of using a gas rich in hydrogen fluoride or in the objective CF_3CF_3 , the organic substance obtained contains CF_3CF_3 as a main component. In the case of
20 using tetrafluoromethane or octafluoropropane as the diluting gas, the gas is purified by again performing distillation. In either case, high-purity CF_3CF_3 can be obtained by repeatedly performing the distillation operation according to the compositional ratio of the
25 organic substance obtained.

 In the distillation for purification of the organic substance, although it may vary depending on the compositional ratio, for example, an inert gas and

CF₄ as the low boiling fraction are extracted from the top of the first distillation tower and the gas mainly comprising CF₃CF₃ is extracted from the bottom and introduced into the second distillation tower. Then, an inert gas and trifluoromethane as the low boiling fraction are extracted from the top of the second distillation tower and the gas mainly comprising CF₃CF₃ is extracted from the bottom and introduced into the third distillation tower to extract high-purity CF₃CF₃ from the top, thereby performing the purification. The gas containing CClF₂CF₃ collected from the bottom in the third distillation may be circulated into the reaction step with hydrogen fluoride of (1).

The thus-purified CF₃CF₃ contains almost no impurities and high-purity CF₃CF₃ can be obtained. The purity thereof is 99.9997 vol% or more, and 1 volppm or less of the compound having chlorine atom and 1 volppm or less of pentafluoroethane are contained as impurities.

As the analysis method of CF₃CF₃ having a purity of 99.9997 vol% or more, gas chromatography (GC) using TCD method, FID method (each including the precut method) or ECD method, or an instrument such as gas chromatography mass spectrometer (GC-MS) may be used.

Use of CF₃CF₃ obtained by the production process of the present invention is described below.

The high-purity CF₃CF₃ can be used as an etching gas at the etching step in the process of manufacturing

a semiconductor device and also can be used as a cleaning gas at the cleaning step in the process of manufacturing a semiconductor device.

5 In the process of manufacturing a semiconductor device such as LSI and TFT, a thin or thick film is formed using CVD, sputtering or vapor deposition, and the film is etched to form a circuit pattern. In the apparatus for forming a thin or thick film, cleaning for removing unnecessary deposits accumulated on the inner wall of the apparatus, jigs and the like is performed, because the produced unnecessary deposits cause generation of particles and must be removed on occasions so as to produce a film having good quality.

10 The etching process using CF_3CF_3 can be performed under various dry etching conditions such as plasma etching and microwave etching, and CF_3CF_3 may be used by mixing it with an inert gas such as He, N_2 and Ar or with a gas such as HCl, O_2 and H_2 at an appropriate ratio.

20

Examples

The present invention is described in greater detail below by referring to the Examples and Comparative Examples, however, the present invention is not limited to these Examples.

25

Raw Material Example 1

In the presence of a fluorination catalyst,

tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$) was reacted with HF at a reaction pressure of 0.4 MPa, a reaction temperature of 300°C and a molar ratio HF/tetrachloroethylene of 4 (first reaction) and then, the reaction was further continued at a reaction pressure of 0.4 MPa, a reaction temperature of 330°C and a molar ratio HF/intermediate ($\text{CF}_3\text{CHCl}_2 + \text{CF}_3\text{CHClF}$) of 4 (second reaction). After the reaction, the removal of acid content and a distillation operation were performed by a conventional method, and the distillate was analyzed by gas chromatography, as a result, crude CF_3CHF_2 (Raw Material 1 of CF_3CHF_2) having a composition shown in Table 2 was obtained.

Table 2

Compound	Purity (vol%)
CF_3CHF_2	99.4513
CH_3Cl	0.0011
CHClF_2	0.0008
CHF_3	0.0224
CClF_3	0.0005
CF_3CClF_2	0.5216
CF_3CHClF	0.0008
$\text{CF}_3\text{CCl}_2\text{F}$	0.0009
$\text{CF}_3\text{CH}_2\text{Cl}$	0.0006

Raw Material Example 2

Raw Material 1 of CF_3CHF_2 obtained by the above-described method was repeatedly distilled by a conventional method, and the distillate was analyzed by gas chromatography, as a result, crude CF_3CHF_2 (Raw Material 2 of CF_3CHF_2) having a composition shown in Table 3 was obtained.

Table 3

Compound	Purity (vol%)
CF_3CHF_2	99.8000
CHClF_2	0.0002
CHF_3	0.0038
CF_3CClF_2	0.1960

Catalyst Example 1

Into a 10 L-volume container containing 0.6 L of pure water, a solution containing 452 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in 1.2 L of pure water and 0.31 L of 28% aqueous ammonia were added dropwise over about 1 hour while stirring under the control to give a reaction solution having a pH of 7.5 to 8.5. The resulting hydroxide slurry was filtrated, thoroughly washed with pure water and then dried at 120°C . The thus-obtained solid was pulverized, mixed with graphite

and then pelletized by a tableting machine. The pellets obtained were calcined at 400°C for 4 hours in a nitrogen stream to obtain a catalyst precursor. This catalyst precursor was filled into an Inconel-made reactor and subsequently subjected to a fluorination treatment (activation of catalyst) at an atmospheric pressure and 350°C in an atmosphere of HF diluted with nitrogen, then in a 100% HF stream, and further at 450°C in an atmosphere of HF diluted with nitrogen to prepare a catalyst.

Catalyst Example 2

Into a 10 L-volume container containing 0.6 L of pure water, a solution containing 452 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 42 g of $\text{In}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (n is about 5) dissolved in 1.2 L of pure water, and 0.31 L of 28% aqueous ammonia were added dropwise over about 1 hour while stirring under the control of respective flow rates of two aqueous solutions to give a reaction solution having a pH of 7.5 to 8.5. The resulting hydroxide slurry was filtrated, thoroughly washed with pure water and then dried at 120°C for 12 hours. The thus-obtained solid was pulverized, mixed with graphite and then pelletized by a tableting machine. The pellets obtained were calcined at 400°C for 4 hours in a nitrogen stream to obtain a catalyst precursor. Into an Inconel-made reactor, the catalyst precursor was filled and subsequently subjected to a fluorination

treatment (activation of catalyst) in the same manner as in Catalyst Example 1 to prepare a catalyst.

(Example 1) Step (1)

5 Into an Inconel 600-type reactor having an inner diameter of 1 inch and a length of 1 m, 150 ml of the catalyst prepared in [Catalyst Example 1] was filled, and the temperature was elevated to 440°C while passing nitrogen. Thereto, hydrogen fluoride was fed at 3.5
10 NL/hr and then Raw Material 1 of CF_3CHF_2 obtained in [Raw Material Example 1] was fed at 3.5 NL/hr. The feeding of nitrogen gas was stopped and the reaction was initiated. After 2 hours, the exhaust gas was washed with an aqueous potassium hydroxide solution to
15 remove the acid content and thereafter, the gas composition was analyzed by gas chromatography, as a result, a gas having a composition shown in Table 4 was obtained.

20

25

Table 4

Compound	Purity (vol%)
CF_3CHF_2	99.3273
CF_4	0.0113
CHF_3	0.0215
CF_3CF_3	0.6120
CF_3CClF_2	0.0156
CF_3CHClF	0.0112
$\text{CF}_3\text{CH}_2\text{Cl}$	0.0011

5 (Example 2) Step (1)

A reaction and an analysis were performed under the same conditions through the same operations as in Example 1 except for filling 150 ml of the catalyst prepared in Catalyst Example 2 as the catalyst. The
10 analysis results are shown in Table 5.

15

Table 5

Compound	Purity (vol%)
CF_3CHF_2	99.2732
CF_4	0.0170
CHF_3	0.0212
CF_3CF_3	0.6720
CF_3CClF_2	0.0068
CF_3CHClF	0.0098
$\text{CF}_3\text{CH}_2\text{Cl}$	0.0015

As is apparent from the analysis results shown in Table 5, when a fluorination catalyst obtained by adding indium to chromium is used, the conversion ratio of CClF_2CF_3 to CF_3CF_3 is improved.

(Example 3) Step (1)

A reaction and an analysis were performed under the same conditions through the same operations as in Example 1 except for changing the reaction temperature to 300°C. The analysis results are shown in Table 6.

Table 6

Compound	Purity (vol%)
CF_3CHF_2	99.4314
CF_4	0.0023
CHF_3	0.0221
CF_3CF_3	0.0387
CF_3CClF_2	0.4829
CF_3CHClF	0.0014
$\text{CF}_3\text{CH}_2\text{Cl}$	0.0005

(Example 4) Step (1)

5 A reaction and an analysis were performed under the same conditions through the same operations as in Example 1 except for changing the reaction temperature to 500°C. The analysis results are shown in Table 7.

10

15

Table 7

Compound	Purity (vol%)
CF ₃ CHF ₂	99.1948
CF ₄	0.1488
CHF ₃	0.0168
CF ₃ CF ₃	0.5880
CHClF ₂	0.0069
CF ₃ CClF ₂	0.0148
CF ₃ CHClF	0.0256
CF ₃ CCl ₂ F	0.0021
CF ₃ CH ₂ Cl	0.0022

(Example 5) Step (1) + Step (2)

5 Into an Inconel 600-type reactor having an inner
diameter of 1 inch and a length of 2 m, 150 ml of the
catalyst prepared in [Catalyst Example 2] was filled,
and the temperature was elevated to 430°C while passing
nitrogen. Thereto, hydrogen fluoride was fed at 5.0
10 NL/hr and then Raw Material 2 of CF₃CHF₂ obtained in
[Raw Material Example 2] was fed at 8.0 NL/hr.
Subsequently, the feeding of nitrogen gas was stopped
and 2 hours after the initiation of the reaction, the
exhaust gas was washed with aqueous potassium hydroxide
15 solution to remove the acid content. The resulting gas
composition was analyzed by gas chromatography, as a
result, a gas having the composition shown in Table 8

was obtained.

Table 8

Compound	Purity (vol%)
CF_3CHF_2	99.7922
CF_4	0.0018
CHF_3	0.0036
CF_3CF_3	0.1980
CF_3CClF_2	0.0008
CF_3CHClF	0.0036

5

The gas having the composition shown in Table 8 after the removal of the acid content was collected under cooling and purified by distillation according to a conventional method. The gas obtained after the purification was analyzed and the results are shown in Table 9.

10

15

20

Table 9

Compound	Purity (vol%)
CF_3CHF_2	99.7950
CF_4	0.0019
CHF_3	0.0035
CF_3CF_3	0.1988
CF_3CClF_2	0.0008

As is apparent from the analysis results shown in
5 Table 9, by performing distillation, chlorotetrafluoro-
ethane can be mostly removed.

Using the gas mainly comprising CF_3CHF_2 after the
purification by distillation obtained above, a direct
fluorination reaction with fluorine gas was performed.

10 An Inconel 600-type reactor having an inner
diameter of 20.6 mm ϕ and a length of 500 mm (using a
heating system by an electric heater; the reactor had
been subjected to a passivation treatment with fluorine
gas at a temperature of 500°C) was heated to a
15 temperature of 420°C while passing nitrogen gas at 30
NL/hr.

Then, hydrogen fluoride was fed at 50 NL/hr, and
into one gas flow diverged from the diluting gas, the
gas mainly comprising CF_3CHF_2 was fed at 3.5 NL/hr.
20 Thereafter, fluorine gas was similarly fed at 3.85 NL/h
to another gas flow diverged from the diluting gas to
perform a reaction. After 3 hours, the reaction

product gas was washed with an aqueous potassium hydroxide solution and an aqueous potassium iodide solution to remove hydrogen fluoride and unreacted fluorine gas. Subsequently, the gas composition was analyzed by gas chromatography. The analysis results are shown in Table 10.

Table 10

Compound	Purity (vol%)
CF_3CHF_2	0.0001
CF_4	0.0456
CF_3CF_3	99.9536
CF_3CClF_2	0.0007

The gas after the removal of the acid content was collected under cooling and purified by distillation. The gas after the purification was analyzed by gas chromatography using TCD method, FID method, ECD method and GC-MS method, and the analysis results are shown in Table 11.

Table 11

Compound	Purity (vol%)
CF ₃ CHF ₂	0.9 volppm
CF ₄	<0.4 volppm
SF ₆	<0.4 volppm
CF ₃ CClF ₂	<0.1 volppm
CF ₃ CF ₂	99.9998 vol%

5 As is apparent from the analysis results shown in Table 11, CF₃CF₃ after the purification contains almost no other impurities, thus, high-purity CF₃CF₃ is obtained and the purity thereof is 99.9997 vol% or more.

10 (Comparative Example 1)

 An Inconel 600-type reactor having an inner diameter of 20.6 mm ϕ and a length of 500 mm (using a heating system by an electric heater; the reactor had been subjected to a passivation treatment with fluorine gas at a temperature of 500°C) was heated to a
15 temperature of 420°C while passing nitrogen gas at 30 NL/h.

 Then, hydrogen fluoride was fed at 50 NL/hr, and into one gas flow diverged from the diluting gas, Raw
20 Material 1 of CF₃CHF₂ obtained in [Raw Material Example 1] was fed at 3.5 NL/hr. Thereafter, fluorine gas was similarly fed at 3.85 NL/h into another gas flow

diverged from the diluting gas to perform a reaction. After 3 hours, the reaction product gas was washed with an aqueous potassium hydroxide solution and an aqueous potassium iodide solution to remove hydrogen fluoride and unreacted fluorine gas. Subsequently, the gas composition was analyzed by gas chromatography. The analysis results are shown in Table 12.

Table 12

Compound	Purity (vol%)
CF ₃ CHF ₂	0.0003
CF ₄	0.0568
CClF ₃	0.0036
CF ₃ CF ₃	99.4160
CF ₃ CClF ₂	0.5233

As is apparent from the analysis results shown in Table 12, when CF₃CHF₂ containing a compound having chlorine atom within the molecule as impurities is reacted with fluorine gas, CClF₃ (chlorotrifluoromethane) which is a substance difficult to separate, is produced.

Then, the gas having the composition shown in Table 12 after the removal of the acid content was collected under cooling and purified by distillation. The gas obtained after the purification was analyzed and the results are shown in Table 13.

Table 13

Compound	Purity (vol%)
CF_3CHF_2	0.0003
CF_4	<0.0001
CClF_3	0.0036
CF_3CF_3	99.9959
CF_3CClF_2	<0.0001

5 As is apparent from the analysis results shown in Table 13, CClF_3 is a compound hard to separate.

EFFECTS OF THE INVENTION

10 As described in the foregoings, by using starting gas mixture containing CF_3CHF_2 and a compound having chlorine atom, high-purity CF_3CF_3 can be produced, and the high-purity CF_3CF_3 produced according to the present invention can be used as an etching gas or a cleaning gas in the process of manufacturing a
15 semiconductor device.

CLAIMS

1. A process for producing hexafluoroethane, comprising the following two steps:

5 (1) a step of reacting a gas mixture containing pentafluoroethane and a compound having chlorine atom with hydrogen fluoride in the gaseous phase in the presence of a fluorination catalyst to fluorinate said compound having chlorine atom; and

10 (2) a step of reacting the gas mixture containing pentafluoroethane and the fluorinated compound obtained in said step (1) with a fluorine gas in the gaseous phase in the presence of a diluting gas.

15 2. The process for producing hexafluoroethane as claimed in claim 1, wherein said compound having chlorine atom is at least one compound selected from the group consisting of chloromethane, chlorotrifluoromethane, chloropentafluoroethane, 20 dichlorotetrafluoroethane, chlorotetrafluoroethane, chlorotrifluoroethane and chlorotrifluoroethylene.

25 3. The process for producing hexafluoroethane as claimed in claim 1 or 2, wherein the total amount of the compound having chlorine atom contained in the gas mixture of the step (1) is 1 vol% or less.

4. The process for producing hexafluoroethane as

claimed in claim 1 or 2, wherein the total amount of the compound having chlorine atom contained in the gas mixture of the step (1) is 0.5 vol% or less.

5 5. The process for producing hexafluoroethane as claimed in any one of claims 1 to 4, wherein in said step (1), the fluorination catalyst is a bulk catalyst obtained by adding indium to an oxide of chromium.

10 6. The process for producing hexafluoroethane as claimed in any one of claims 1 to 5, wherein in said step (1), the temperature at the reaction with hydrogen fluoride in the presence of a fluorination catalyst is in the range of 150 to 480°C.

15 7. The process for producing hexafluoroethane as claimed in any one of claims 1 to 6, wherein in said step (1), the molar ratio of hydrogen fluoride/organic substance contained in the gas mixture is in the range
20 of 0.5 to 5.

8. The process for producing hexafluoroethane as claimed in any one of claims 1 to 7, wherein a step of removing an acid content containing hydrogen chloride
25 produced is conducted before said step (2).

9. The process for producing hexafluoroethane as claimed in any one of claims 1 to 8, wherein a step of

separating chlorotetrafluoroethane and/or chlorotri-
fluoroethane, and returning the chlorotetrafluoroethane
and/or chlorotrifluoroethane separated to the step (1)
is conducted before said step (2).

5

10. The process for producing hexafluoroethane as
claimed in any one of claims 1 to 9, wherein in said
step (2), the total amount of the compound having
chlorine atom contained in the gas mixture is 0.02 vol%
or less.

10

11. The process for producing hexafluoroethane as
claimed in any one of claims 1 to 10, wherein in said
step (2), the fluorinated compound contained in the gas
mixture is mainly composed of hexafluoroethane.

15

12. The process for producing hexafluoroethane as
claimed in any one of claims 1 to 11, wherein in said
step (2), the diluting gas is a gas containing at least
one selected from the group consisting of
tetrafluoromethane, hexafluoroethane, octafluoropropane
and hydrogen fluoride.

20

13. The process for producing hexafluoroethane as
claimed in any one of claims 1 to 12, wherein in said
step (2), the diluting gas is a gas rich in hydrogen
fluoride.

25

14. The process for producing hexafluoroethane as claimed in any one of claims 1 to 13, wherein in said step (2), the temperature at the reaction of gas mixture containing the fluorinated compound with
5 fluorine gas is in the range of 250 to 500°C.

15. The process for producing hexafluoroethane as claimed in any one of claims 1 to 14, wherein in said step (2), the temperature at the reaction of gas
10 mixture containing the fluorinated compound with fluorine gas is in the range of 350 to 450°C.

16. A hexafluoroethane product comprising hexafluoroethane having a purity of 99.9997 vol% or
15 more.

17. The hexafluoroethane product as claimed in claim 16, wherein the content of the compound having chlorine atom is 1 volppm or less and the content of the
20 pentafluoroethane is 1 volppm or less.

18. An etching gas comprising the hexafluoroethane product described in claim 16 or 17.

25 19. A cleaning gas comprising the hexafluoroethane product described in claim 16 or 17.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 December 2001 (27.12.2001)

PCT

(10) International Publication Number
WO 01/98240 A3

(51) International Patent Classification⁷: C07C 19/08,
17/20, 17/10, 17/395

(74) Agent: SUZUKI, Shunichiro; SUZUKI & ASSO-
CIATES, Gotanda Yamazaki Bldg. 6F, 13-6, Nishigotanda
7-chome, Shinagawa-ku, Tokyo 141-0031 (JP).

(21) International Application Number: PCT/JP01/05256

(22) International Filing Date: 20 June 2001 (20.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2000-185654 21 June 2000 (21.06.2000) JP
60/230,806 7 September 2000 (07.09.2000) US

(71) Applicant (for all designated States except US): SHOWA
DENKO K.K. [JP/JP]: 13-9, Shibadaimon 1-chome, Mi-
nato-ku, Tokyo 105-8518 (JP).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA,
ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): OHNO, Hiromoto
[JP/JP]: c/o KAWASAKI PLANT, SHOWA DENKO
K.K., 5-1, Ogimachi, Kawasaki-ku, Kawasaki-shi, Kana-
gawa 210-0867 (JP). KAGA, Kazunari [JP/JP]: c/o
KAWASAKI PLANT, SHOWA DENKO K.K., 5-1, Ogi-
machi, Kawasaki-ku, Kawasaki-shi, Kanagawa 210-0867
(JP). OHI, Toshio [JP/JP]: c/o KAWASAKI PLANT,
SHOWA DENKO K.K., 5-1, Ogimachi, Kawasaki-ku,
Kawasaki-shi, Kanagawa 210-0867 (JP).

Published:

— with international search report

(88) Date of publication of the international search report:
6 June 2002

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

WO 01/98240 A3

(54) Title: PROCESS FOR PRODUCING HEXAFLUOROETHANE AND USE THEREOF

(57) Abstract: The present invention intends to provide a process for producing CF_3CF_3 with good profitability using CF_3HF_2 containing a compound having chlorine atom within the molecule, and use thereof. In the process of the present invention, a gas mixture containing CF_3CHF_2 and a compound having chlorine atom within the molecule is reacted with hydrogen fluoride in the presence of a fluorination catalyst, thereby converting CClF_2CF_3 as a main impurity into CF_3CF_3 , and CF_3CHF_2 containing CF_3CF_3 is reacted with fluorine gas in the gaseous phase in the presence of a diluting gas.

INTERNATIONAL SEARCH REPORT

Intel. Application No

PCT/JP 01/05256

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C19/08 C07C17/20 C07C17/10 C07C17/395

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 612 709 A (ATOCHEM ELF SA) 31 August 1994 (1994-08-31) claims	1-19
Y	US 5 710 351 A (NAKAJO TETSUO ET AL) 20 January 1998 (1998-01-20) claims	1-19
Y	GB 2 311 522 A (SHOWA DENKO KK) 1 October 1997 (1997-10-01) claims	1-19
Y	WO 99 31032 A (DAIKIN IND LTD) 24 June 1999 (1999-06-24) claims -& EP 1 038 858 A (DAIKIN IND LTD) 27 September 2000 (2000-09-27) page 2, line 14 - line 15; claims 1-11	1-19
	-/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

13 March 2002

Date of mailing of the international search report

21/03/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bonnevalle, E

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 01/05256

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	"METHODS FOR SEPARATING CHLORO-CARBONS FROM HYDROFLUOROALKANES" RESEARCH DISCLOSURE, KENNETH MASON PUBLICATIONS, HAMPSHIRE, GB, no. 360, 1 April 1994 (1994-04-01), pages 191-193, XP000446558 ISSN: 0374-4353 page 191 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 01/05256

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0612709	A	31-08-1994	FR 2701943 A1 AU 652321 A1 CA 2115975 A1 CN 1099022 A DE 69400036 D1 DE 69400036 T2 EP 0612709 A1 ES 2081226 T3 JP 6256234 A US 5453551 A	02-09-1994 18-08-1994 25-08-1994 22-02-1995 18-01-1996 18-07-1996 31-08-1994 16-02-1996 13-09-1994 26-09-1995
US 5710351	A	20-01-1998	JP 9241186 A DE 19654720 A1 GB 2311287 A ,B CN 1165803 A ,B SG 48501 A1 TW 409114 B	16-09-1997 11-09-1997 24-09-1997 26-11-1997 17-04-1998 21-10-2000
GB 2311522	A	01-10-1997	JP 3067633 B2 JP 9255598 A DE 19654719 A1	17-07-2000 30-09-1997 02-10-1997
WO 9931032	A	24-06-1999	JP 11171806 A EP 1038858 A1 WO 9931032 A1	29-06-1999 27-09-2000 24-06-1999